

# CANADA

## THE PATENT OFFICE

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### Stabilization of Printing Pastes Containing Diazonium Salts

Frederic H. Adams, Bound Brook, New Jersey,  
U.S.A., assignor to American Cyanamid Company,  
New York, New York, U.S.A.

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No Drawing

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This invention relates to compositions containing ice colour diazo components, diazotized or undiazotized, and to methods of preventing the thinning of printing pastes containing such diazo components.

Producing prints of ice colours on various vegetable fibres often is effected by padding the goods with an alkaline solution of an azoic coupling component and printing with a printing paste containing diazotized ice colour diazo components either freshly prepared or in the form of stabilized diazonium salts. This is a well-known cheap process for producing azoic prints and requires no difficult treatment. However, it is open to a very serious disadvantage. The printing pastes containing the diazonium salts, stabilized or unstabilized, do not keep well and particularly tend to thin out rapidly, losing their desired printing consistency. It is this thinning action with which the present invention is concerned.

According to the present invention the diazonium salt, either in stabilized form or freshly prepared, is associated with a water soluble acid amide in which at least one of the amide hydrogens is replaced by an organic radical having at least one olefinic double bond or an acetylenic triple bond.

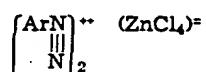
When an aromatic amine is diazotized in acid solution, a diazonium salt is formed which is generally assumed to have the following formula:



where Ar stands for the aromatic radical of the diazo component and X stands for the anion of the acid. These diazonium salts are salts of the very strong diazonium bases and the aqueous solutions contain essentially the diazonium cations and the anions of the acid used, as indicated by the formula. Some of these diazonium salts are difficult to isolate because of their great solubility. Others are not so soluble and can be easily isolated. Some are difficult to handle after isolation because of their explosiveness; others are rather stable and do not present an explosive hazard. It is also known that if the anion of the acid X<sup>-</sup> is properly chosen, in almost all cases diazonium salts of lower solubility may be produced and therefore isolated, and it is also known that many of these diazonium salts have lost their explosive character and can be stored and handled in the dry state without danger; this kind of diazonium salt is sometimes referred to as "stabilized" diazonium salts. They comprise such compounds as certain aromatic sulphonates,

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without olefinic double bonds, borofluorides, and particularly salts of complex acids sometimes referred to as double salts, the most important of them being the double salts of diazonium chlorides and zinc chloride which correspond to the formula:



It should be borne in mind that also these "stabilized" diazonium salts including the above-mentioned double salts are true diazonium salts, i.e. the aqueous solution contains the same diazonium cations as the solution of any other diazonium salt derived from the same base.

The present invention deals with inhibiting the thinning action of diazonium salts only and not with any similar action that might be observed with other types of diazo compounds. While it is not intended to limit the present invention to any theory of action, we believe that it is highly probable that lowering of viscosity of printing gums is essentially caused by the diazonium cation because the same kind of thing results regardless of the anion of the diazonium salt and even the double salts of the stabilized diazonium salts described above exert a similar thinning action. Presumably in aqueous solution the stabilized diazonium salts are ionized to give the same diazonium cation. The pH of the printing paste is not critical so long as it is on the acid side for the present invention does not deal with any other types of pastes. Alkaline medium, as is well known, causes rearrangement of the diazonium salts to diazo compounds of different structure.

While not desiring to limit the invention thereto, we believe that the evidence strongly indicates that the thinning action is a colloidal phenomenon rather than a chemical reaction. The following test was made:

A diazonium salt derived from 2-nitro-4-methoxy aniline was added to a printing paste made up with a starch thickener; after 20 hours the then water-thin solution was coupled with an alkaline solution of beta-naphthol and the azo dye formed was removed by filtration. The amount of azo dyestuff obtained indicated that the bulk of the diazonium salt was undecomposed and had reacted while the filtrate still showed the reaction of starch and not the reactions of reducing sugars.

The thinning action differs widely and depends upon the structure of the diazo component the diazonium salt derives from. We have found that those diazonium salts that are known to be very

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The solution of bis-N-allylamido phosphoric acid used in this example is prepared as follows:

20 parts of allylamine in 60 parts of dry ether are added with stirring to 15.34 parts of phosphorus oxychloride in a vessel cooled externally by ice. After stirring for an hour at room temperature the precipitate of allylamine hydrochloride is filtered off, and the ether is evaporated from the filtrate. The viscous oil remaining is reacted with 20 parts of water, with which it reacts vigorously. The resulting clear solution is made alkaline to Brilliant Yellow paper by a solution containing 4 parts of caustic soda, and the excess allylamine is distilled off with steam. The slightly acid residual solution contains the thinning inhibitor and is used as such without isolation of the active ingredient.

## Example 10

An intimate mixture is made of 1.68 parts of 3-nitro-4-amino anisole, 0.84 part of N-allyl succinamic acid, and 0.84 part of common salt. This mixture is stirred with 15 parts of water, 6.5 parts of 5N hydrochloric acid and enough ice to lower the temperature to 5°C., and the base is diazotized by the addition of 0.7 part of sodium nitrite dissolved in approximately two parts of water. The mixture is stirred at 5-10°C. until diazotization is complete, and then diluted to a volume equal to that occupied by 50 parts of water. One printing paste is made by thoroughly mixing one-half of the diazo solution prepared above with 75 parts of 2.5% carob bean gum; another printing paste is made by mixing one-half of the above-prepared diazo solution with 75 parts of 8% starch paste made from the brand of starch powder known to the trade as RPG Gum. These printing pastes become thin much less rapidly than similar pastes prepared from equivalent amounts of the same base not mixed with thinning inhibitor. For this reason, the printing pastes described above retain their utility for the printing of fast colour patterns on cloth impregnated with ice colour coupling components for a longer time than pastes which do not contain the inhibitor. This is shown in the following table. The relative viscosity measurements indicated below are the times in seconds for copper plated steel shot of the weight indicated to fall 130 millimetres through the paste.

Thinning Inhibitor Used	Gum Used	Relative Viscosity Reading 2/4 Min.	Relative Viscosity Reading 1 Hour	Relative Viscosity Reading 18 Hours	Weight of Shot Used
N-allyl succinamic acid	2.5% carob bean	65.4	63.6	25.2	0.107
None	"				"
N-allyl succinamic acid	8% RPG starch gum	62.2	20.4	1.0	0.358 g.
None	"	9.2	7.0	4.0	
		14.2	5.0	1.6	"

I claim:

**Claim.—1.** A composition suitable for forming printing pastes, comprising an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing a carbohydrate thickener and water soluble diazonium salts derived from ice colour diazo components, the colour forming component having admixed therewith a water soluble acid amide having at least one amide hydrogen

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replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid being sufficient to substantially inhibit thinning of the paste.

**2.** A composition suitable for forming printing pastes, comprising an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing a carbohydrate thickener and water soluble diazonium salts derived from ice colour diazo components, the colour forming component having admixed therewith a water soluble acid amide of a carboxylic acid having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

**3.** A composition suitable for forming printing pastes, comprising an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing a carbohydrate thickener and water soluble diazonium salts derived from ice colour diazo components, the colour forming component having admixed therewith a water soluble acid amide of an organic sulphonlic acid having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning

of the paste.

**4.** A composition suitable for forming printing pastes, comprising an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing a carbohydrate thickener and water soluble diazonium salts derived from ice colour diazo components, the colour forming component having admixed therewith a water soluble acid amide of an inorganic acid having at least one

amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

5. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a water soluble acid amide having at least one of the amide hydrogens replaced with an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals having an acetylenic triple bond, the amides being free from groups capable of azoic coupling or reacting with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature.

6. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a water soluble acid amide of a carboxylic acid having at least one of the amide hydrogens replaced with an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals having an acetylenic triple bond, the amides being free from groups capable of azoic coupling or reacting with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature.

7. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a water soluble acid amide of an organic sulphonate acid having at least one of the amide hydrogens replaced with an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals having an acetylenic triple bond, the amides being free from groups capable of azoic coupling or reacting with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature.

8. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a water soluble acid amide of an inorganic acid having at least one of the amide hydrogens replaced with an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals having an acetylenic triple bond, the amides being free from groups capable of azoic coupling or reacting with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature.

9. A printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo compound and a water soluble acid amide having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable

of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

10. A printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo compound and a water soluble acid amide of a carboxylic acid having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

15. A printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo compound and a water soluble acid amide of an organic sulphonate acid having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

20. A printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo compound and a water soluble acid amide of an inorganic acid having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste.

25. A composition according to claim 1 in which the organic radical replacing at least one of the hydrogens of the amide group contains an olefinic double bond.

30. A composition according to claim 5 in which the organic radical replacing at least one of the hydrogens of the amide group contains an olefinic double bond.

35. A composition according to claim 9 in which the organic radical replacing at least one of the hydrogens of the amide group contains an olefinic double bond.

40. A process of stabilizing printing pastes containing a carbohydrate thickener and a diazonium salt derived from an ice colour diazo component which comprises incorporating into the paste a sufficient amount of a water soluble acid amide having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo

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compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste by the diazonium salt.

17. A process of printing fabrics containing ice colour coupling components with a printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component and a water soluble acid amide having at least one amide hydrogen replaced by an organic radical included in the group consisting of organic radicals having at least one olefinic double bond and organic radicals containing an acetylenic triple bond, the acid amide being free from groups capable of azoic coupling or of reaction with nitrous acid and also being free from metal compounds capable of decomposing diazo compounds at room temperature, the amount of the acid amide being sufficient to substantially inhibit thinning of the paste by the diazonium salt. 20

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18. A composition according to claim 2 in which the water soluble acid amide is N-allyl acetamide.

19. A composition according to claim 2 in which the water soluble amide is an N-allyl oxamic acid compound.

20. A composition according to claim 2 in which the water soluble acid amide is an N-allyl succinamic acid compound.

SMART & BIGGAR,  
Victoria Bldg.,  
Ottawa, Ont.,  
Patent Agent  
of the Applicant.